



ADVANCED REACTOR SAFEGUARDS

Flow-Enhanced Sensors for MSRs

Assessment of Actinide Quantification Capabilities

PRESENTED BY

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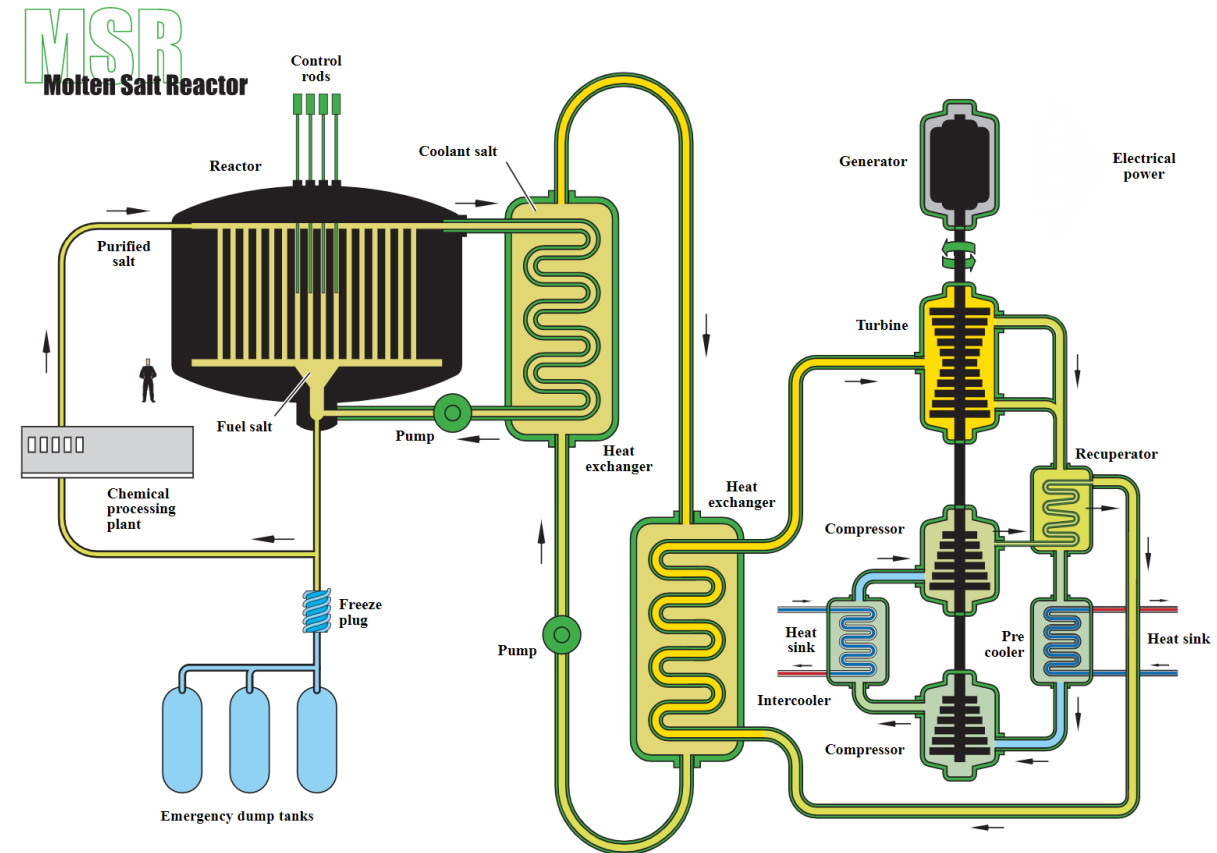
Safeguards and Process Monitoring for Molten Salt Reactors



The dissolved actinides within fuel salts make MSRs a challenge for safeguards

- High temperatures and corrosive salts make it difficult to design sensors with sufficient longevity, stability, and accuracy
- Simple flush-out accountancy is difficult to implement
- Rapid detection of concentration or salt level changes needed to identify diversion
- Operator readable sensor output necessary to detect anomalies

The goal of the Advanced Reactor Safeguards project is to provide MSR vendors the technologies needed to meet broad NRC licensing challenges for materials accountancy.



DOE Gen4 Road Map (downloaded from:
http://www.ne.doe.gov/genIV/documents/gen_iv_roadmap.pdf)

Monitoring and Control of Molten Salt Systems

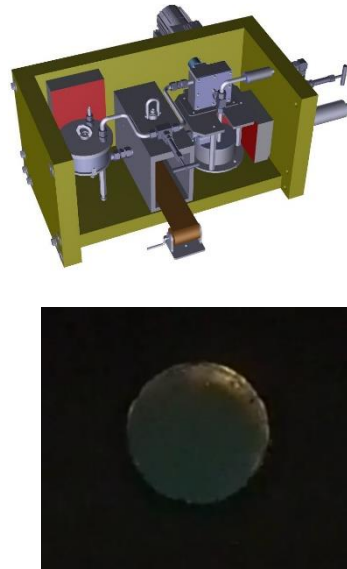


Argonne has demonstrated monitoring for a variety of molten salt equipment including thermal convection loops, salt purification equipment, and process vessels. Deployable sensors for composition, redox state, particle concentrations, etc. have been created.

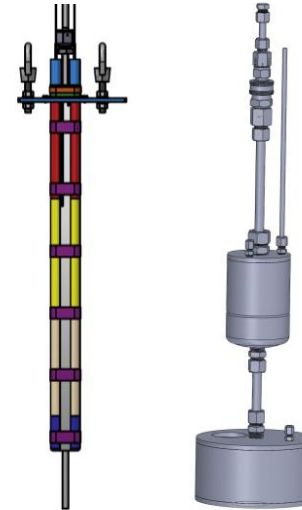
Electrochemical Monitoring of Salt Composition¹



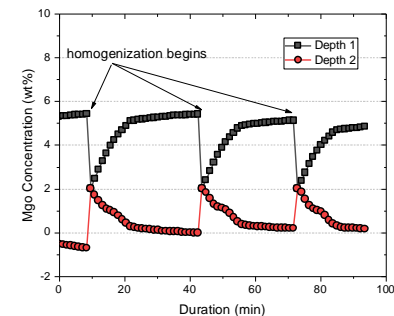
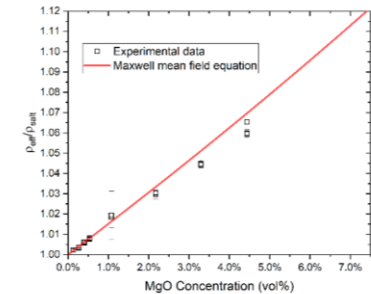
Windowless Optical Monitoring of Salt Composition²



Automated Salt Sampling²



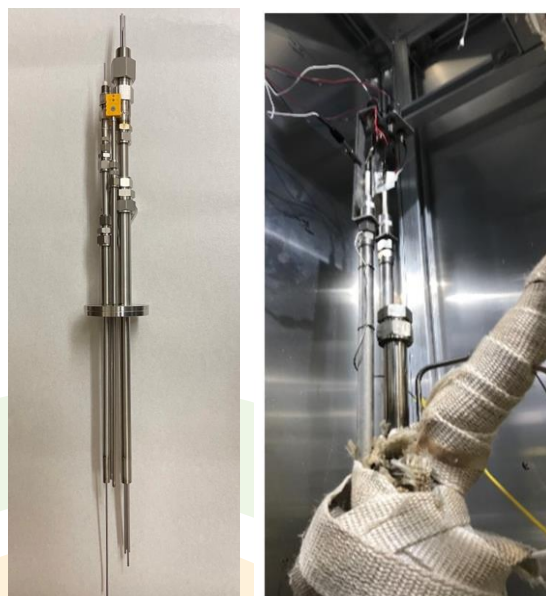
Monitoring of Precipitated Particles³



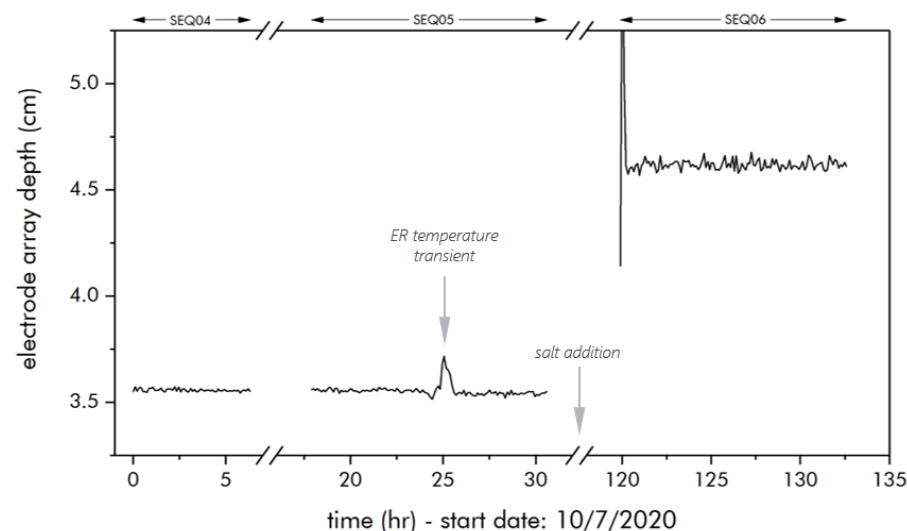
Molten Salt Monitoring



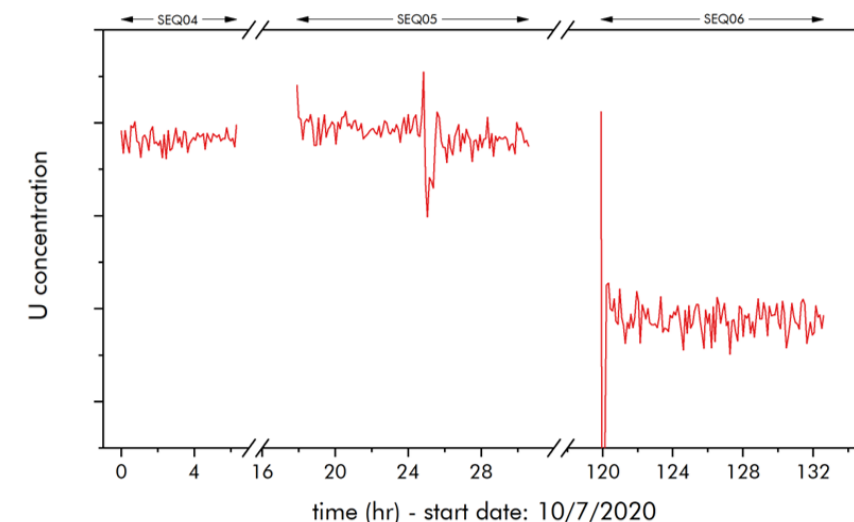
Argonne has operated electrochemical sensors for years-long durations in fuel reprocessing equipment and thermal convection loops. However, none of these previous probes were specifically designed be directly installed in flowing conditions.



Typical multi-electrode array sensor

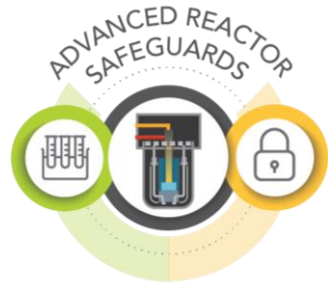


Electrode array depth versus time during period the salt addition



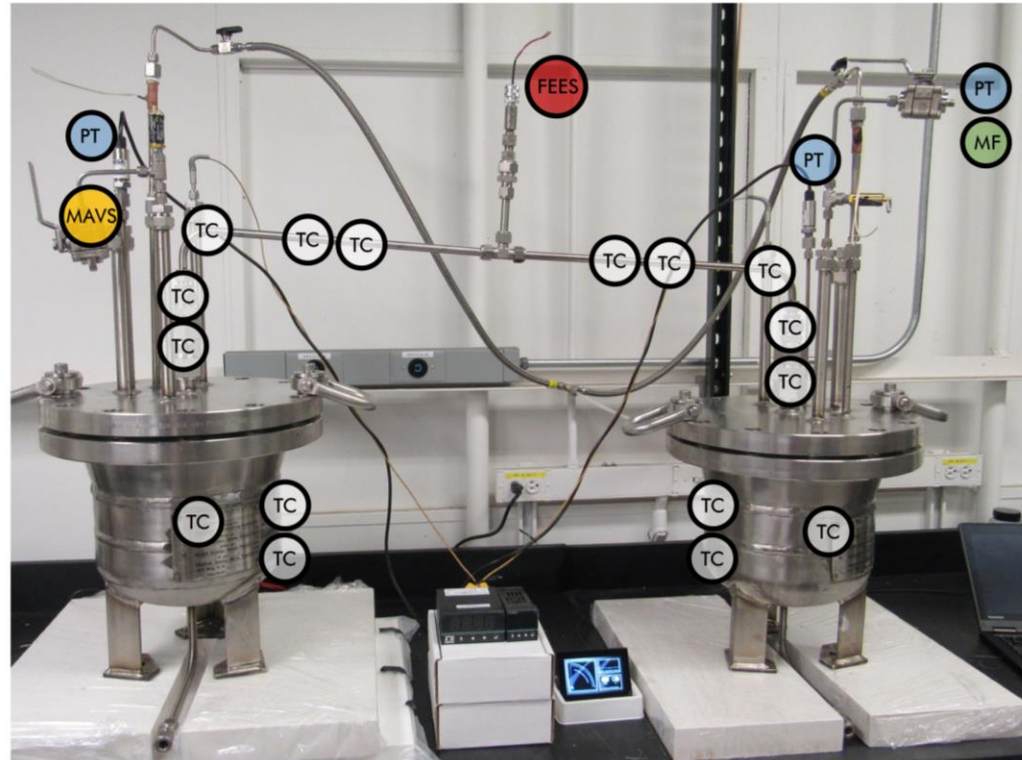
U concentration versus time during the salt addition

Modular Flow Instrumentation Testbed (MFIT)



We built a modular instrumentation testbed in order to develop and assess a variety of molten salt sensors in flowing conduits

- Enables rapid assessment of new sensor designs
- Supports radiological and non-radiological salts
- Supports a wide variety of instrumentation
- Permits rapid salt changes (chlorides, fluorides)
- Flow rates (0.01 to 1 L/s) and transfer line sizes (1/4" to 1") to achieve conditions representative of bypass lines, sampling lines, and flow conduits
- Non-radiological operations: 3 months in total
- Radiological operations: >9 months in total



Flow-Enhanced Electrochemical Sensor



Multielectrode Array Voltammetry Sensor



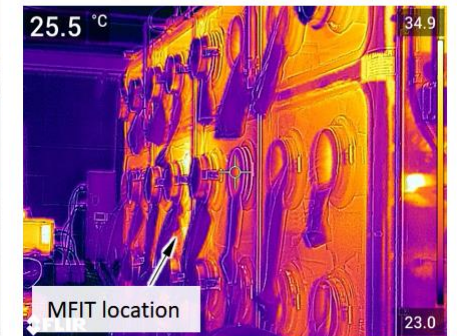
Thermocouple



Pressure Transducer



Mass Flow Meter

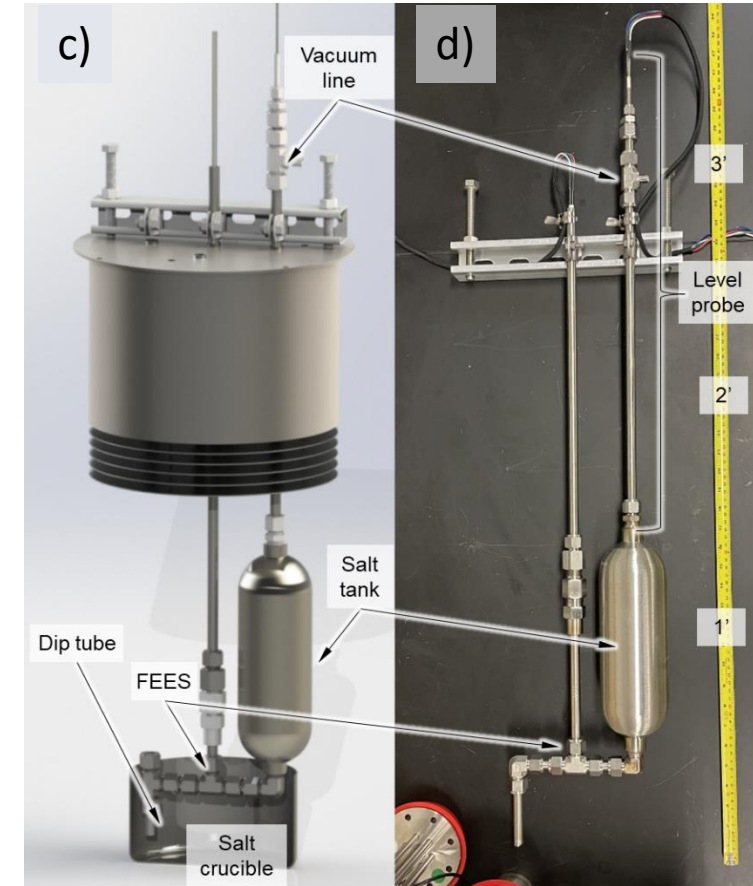
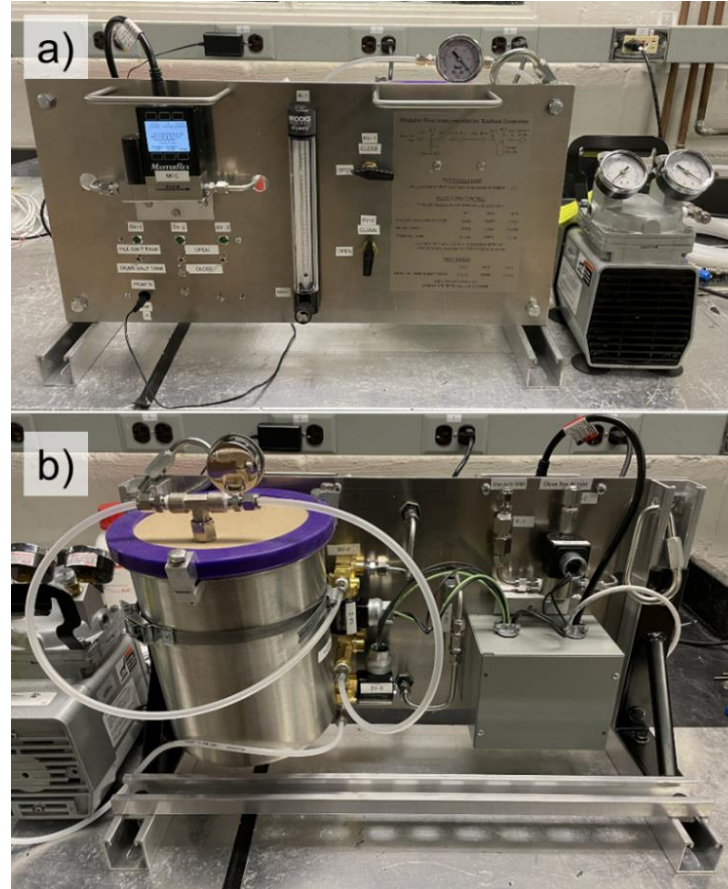


In-Well Mini-MFIT Flow System



A miniaturized in-well MFIT was also built in order to increase sensor development throughput

- Operated remotely using fully automated control panel
- Manual operational mode is available
- Enables rapid assessment of new sensor designs
- Fits into furnace well for ease of disassembly/salt change



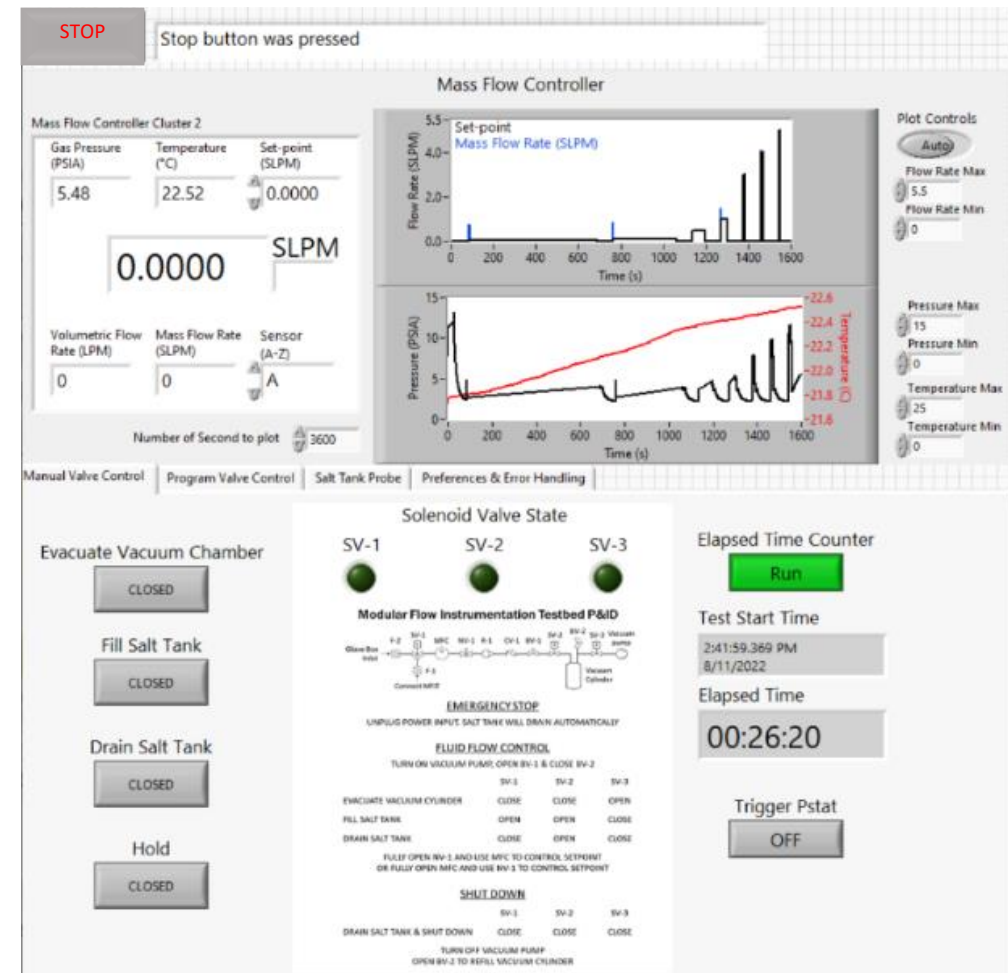


Automation of Measurements and Analysis

During FY22 and FY23 we developed a fully automated system for operating the MFIT and acquiring sensor data

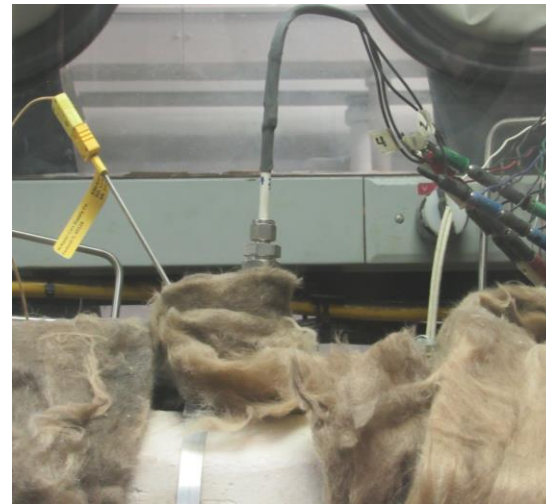
- Capabilities for automated salt transfers with accompanying triggering of sensor systems
- Real time display of system parameters (T, P, etc.)
- Hands-free use enables accelerated sensor assessments

The safeguards sensor framework is being developed to enable complete multi-modal monitoring for molten salt systems

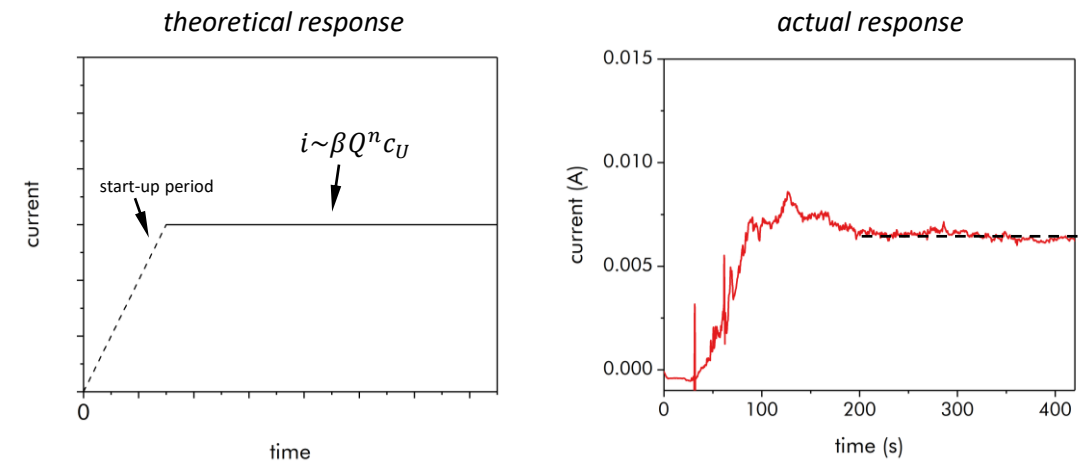


Actinide Measurements in Flowing Salts

Argonne conducted an actinide measurement campaign in FY22. Experiments involved 4 kg of $\text{MgCl}_2\text{-KCl-NaCl-UCl}_x$ salt. Hundreds of salt transfers were made during testing across a range from 1 L/min to 10 L/min



Sensor response to soluble-soluble reactions



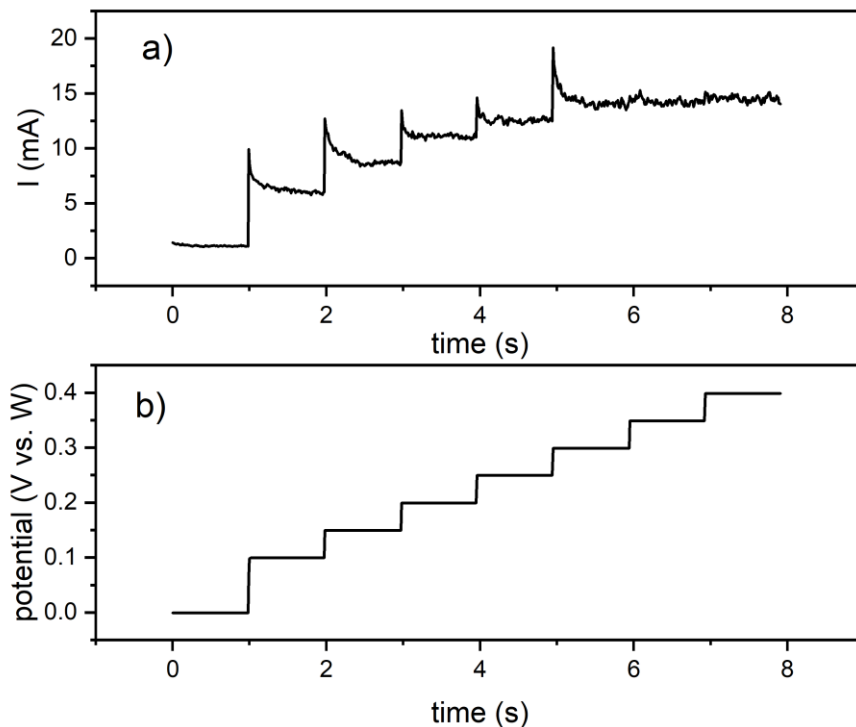
Salt transfer tank (left) and flow-enhanced electrochemical sensor installed into transfer line (right)

Theoretical (left) and actual (right) current response for soluble-soluble reaction

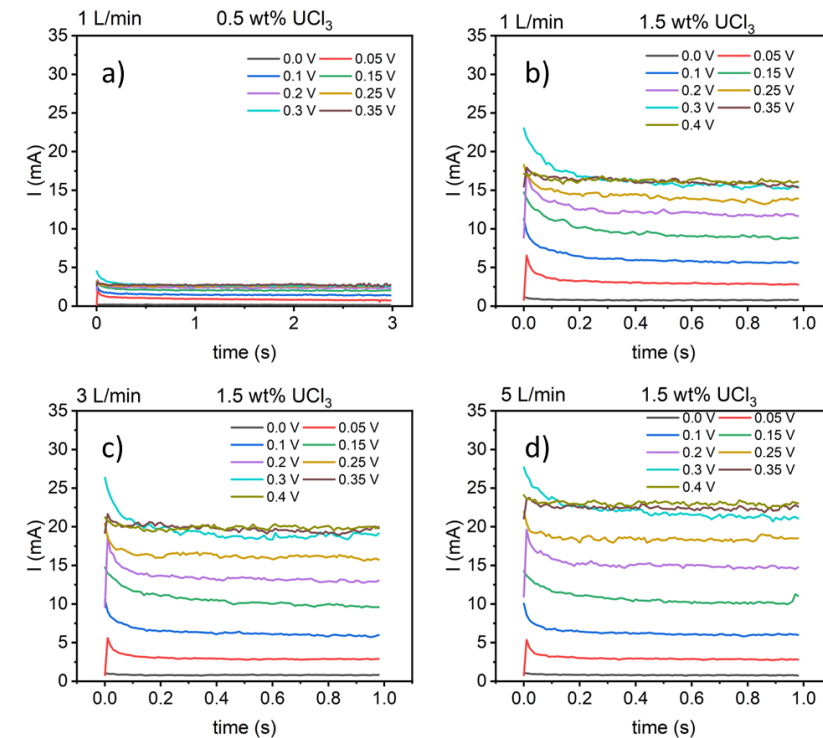
Actinide Measurements in Flowing Salts



The flowing conditions enable electrochemical approaches such as long-duration staircase voltammetry waveforms. These extended waveforms allow for discrimination and quantification of multiple soluble-soluble reactions



U^{3+}/U^{4+} current response to staggered potential holds during a single salt transfer.



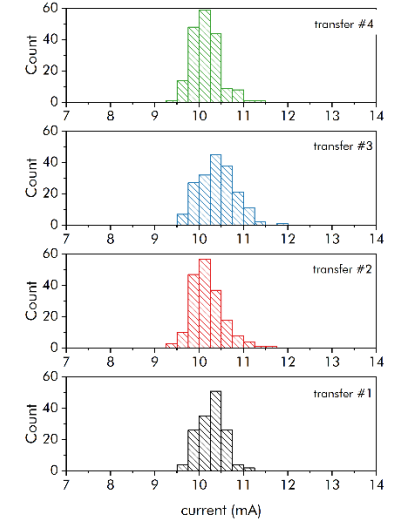
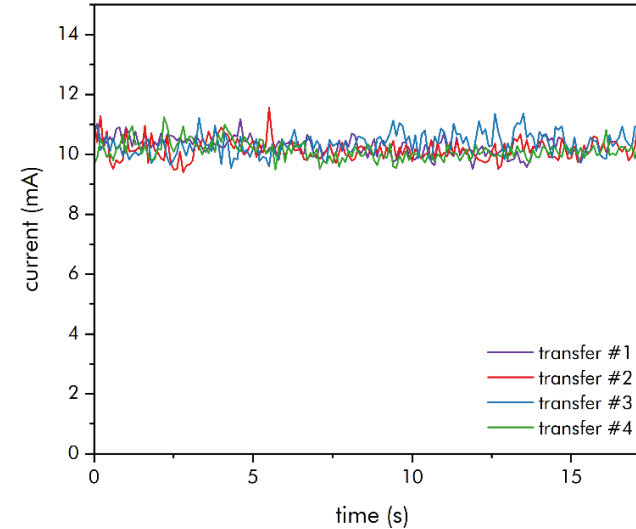
Current response of multiple potential holds during a single flow experiment using the FEES. UCl_3 concentration was 0.5 (a) and 1.5 (b, c, and d)



Repeatability over Extended Testing

Sensor measurements were found to be highly repeatable across multiple salt transfers.

- Statistical analyses showed low standard deviation within single runs and a relative standard deviation of 0.97% between runs
- Long term testing (9 months) of the sensor indicated robustness similar to quiescent salt sensors
 - Hundreds of transfers were completed during this timeframe



	Transfer #1	Transfer #2	Transfer #3	Transfer #4
Mean Current (mA)	10.28	10.15	10.36	10.12
Standard Deviation (mA)	0.304	0.354	0.384	0.313
Confidence Interval (99.0%) (mA)	0.0653	0.0759	0.0823	0.0671

Metric	Value from Repeated Transfers
Mean Current (mA)	10.23 mA
Relative Standard Deviation	0.97%
Confidence Level (99.0%) (mA)	0.23 mA

Current Response to Flow Conditions

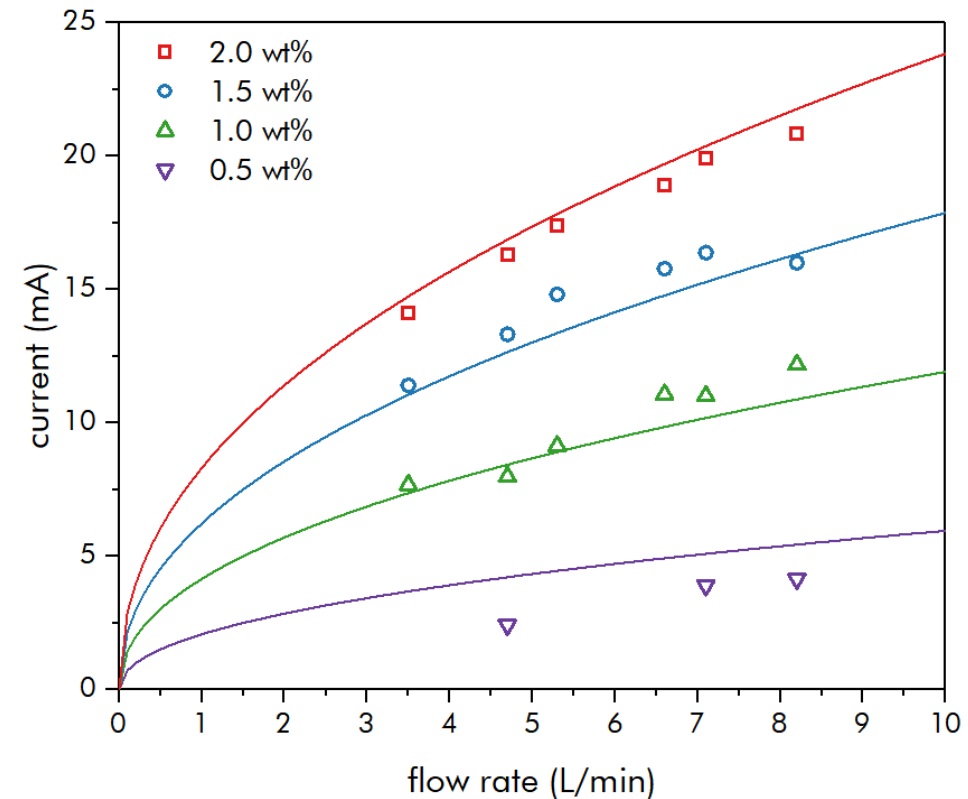
The sensor response with respect to flow rate has been found to vary in a manner consistent with standard mass transfer correlation (i.e., Sherwood numbers)

$$Sh = kRe^m Sc^{1/3}$$

Once developed, the Sherwood number correlations allows for accurate concentration measurements

$$i = \beta Q^n \Delta C$$

$$\beta = \frac{(\pi/4)^{1-m} d D_i z F k Sc^{1/3}}{\rho} \left(\frac{\rho}{\mu d_0} \right)^m$$

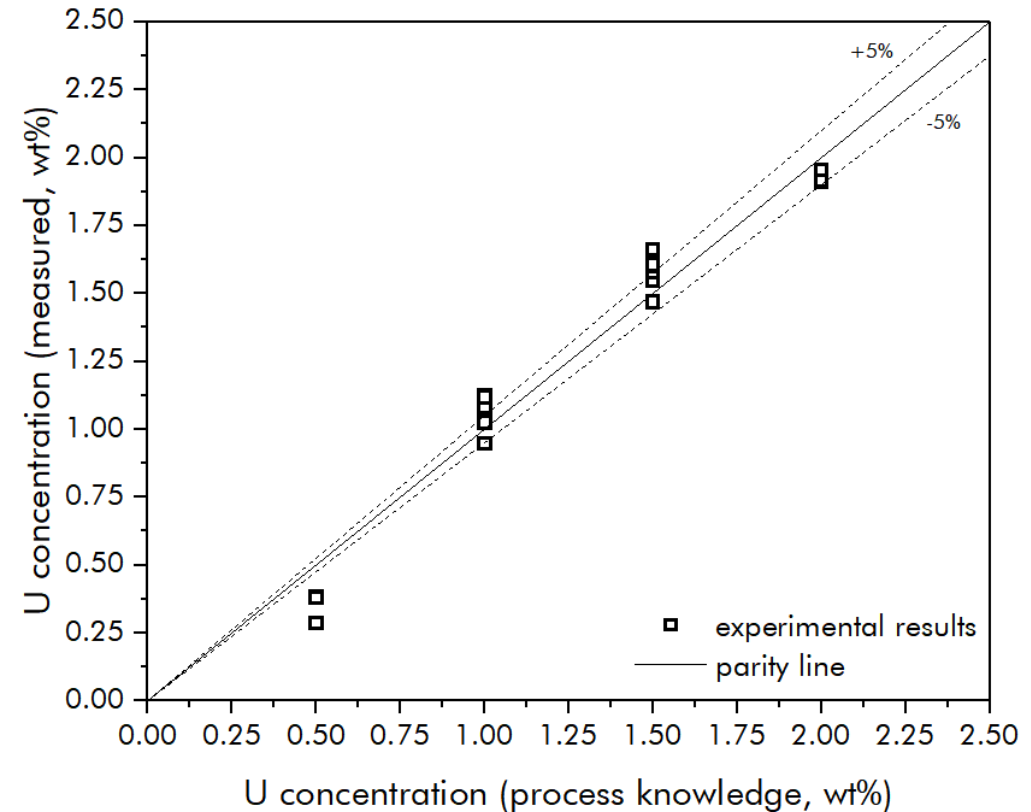


Constant current measurements at various observed flow rates. Measurements taken at four UCl_3 concentrations (0.5, 1.0, 1.5, and 2.0 wt%) in $MgCl_2$ -KCl-NaCl at 500 °C.

Concentration Measurements

Uranium concentration measurements have been found to closely follow the expected parity line.

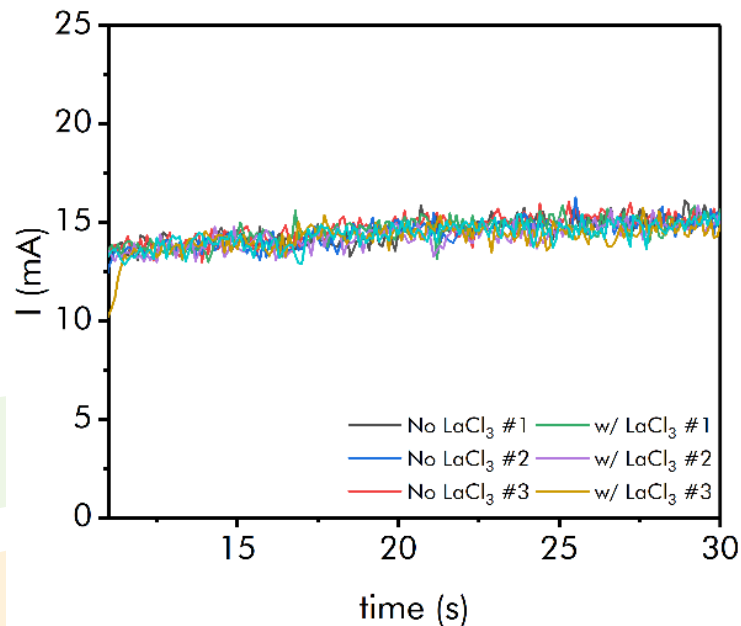
- Most measurements were within $\pm 5\%$ of process knowledge
- Deviation at low concentrations was likely due to an oxygen/moisture ingress which generated UO_2 particles
- Further testing is taking place to improve the accuracy of the sensor



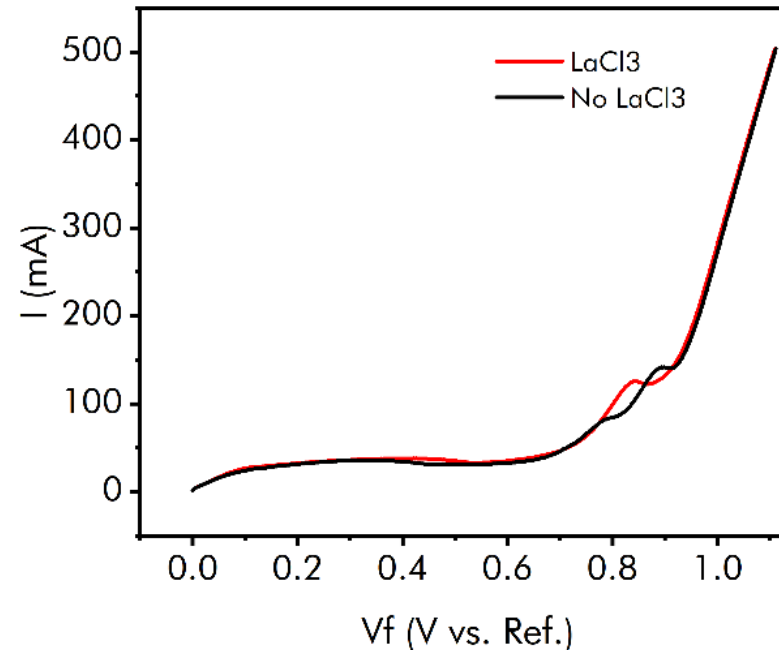
U concentration measured with flow sensor vs. U concentration from process knowledge. Dotted lines are parity $\pm 5\%$.

Tests with Surrogate Fission Products

Tests with surrogate fission products showed that the concentration measurements for UCl_3 based on the $\text{U}^{3+}/\text{U}^{4+}$ reaction were unaffected by the inclusion of additional species.



Chronoamperometry using the FEES at 5.3 L/min before and after 0.25 wt% LaCl_3 addition (overlapping).



LSVs taken with the MAVS before (black) and after (red) LaCl_3 addition. Measurements were made in MgCl_2 -KCl-NaCl containing 2.0 wt% UCl_3

	$\text{U}^{3+}/\text{U}^{4+}$ plateau current (average from 3× transfers)	Measured Uranium Concentration (average from 3× transfers)
Prior to LaCl_3 addition	14.73 ± 0.35 mA	1.65 ± 0.04 wt%
After LaCl_3 addition	14.53 ± 0.27 mA	1.63 ± 0.03 wt%



Tank Sensor Results

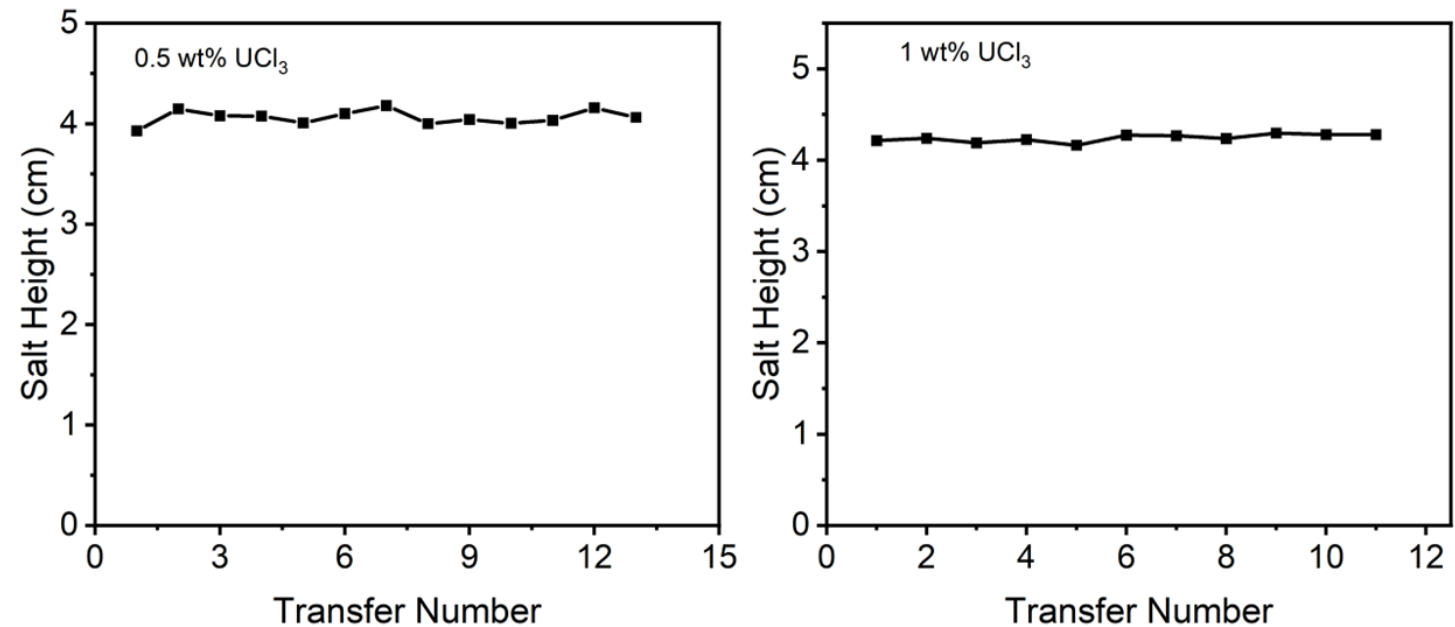
Information from the transfer tank sensors has also been examined.

Salt level measurements were found to be repeatable across multiple salt transfers

- Relative standard deviation of 1.5% for tank-to-tank transfers

Studies of tank inventory will be performed in FY23

- Additional level measurement sensors based on ultrasonics are being integrated into the system for FY23.

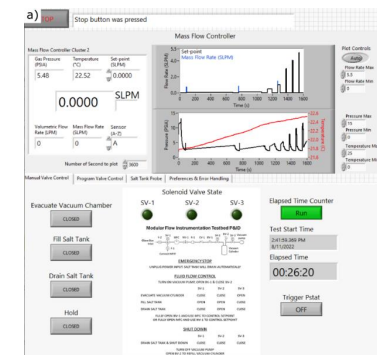


Salt height measurements made with the MAVS during multiple transfer experiments using the MFIT system.

Conclusions



- The MFIT was operated at temperature for more than 9 months
 - Non-rad and radiological measurement campaigns have been completed
 - Upgraded electrochemical sensors were shown to have good accuracy even across a wide range of flow conditions
- During FY23, the system was made to be fully automated and is now being prepared for additional measurement campaigns
 - Improvements to electrochemical sensor accuracy are being pursued
- Further upgrades including multimodal sensor triggering and analysis are planned for the second half of FY23



Acknowledgements



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